Japanese Kokai Patent Application No. Hei 2[1990]-111703

JAPANESE PATENT OFFICE
PATENT JOURNAL (A)
KOKAI PATENT APPLICATION NO. HEI 2[1990]-111703

Int. Cl.[5]:	A 01 N 25/04 25/22
Sequence No. for Office Use:	7043-4H
Filing No.:	Sho 63[1988]-264489
Filing Date:	October 19, 1988
Publication Date:	April 24, 1990
Number of Claims:	1 (Total 6 pages)
Examination Request:	Not filed

AGROCHEMICAL SUSPENSION PREPARATION

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[There are no amendments to this patent.]

Claim

An agrochemical suspension preparation characterized in that it is formed by blending a surfactant, water-soluble biopolymer and water-soluble polymer having carboxy groups with a raw water-insoluble or hard-to-dissolve agrochemical to suspend said raw agricultural chemical in water, while containing 0.02-0.5 wt% of the aforementioned water-soluble biopolymer and 0.05-5 wt% of the aforementioned water-soluble polymer.

Detailed explanation of the invention

This invention pertains to an agrochemical suspension preparation having excellent suspension stability, fluidity and self-dispersing properties.

Prior art

Conventionally, agrochemical products are prepared and applied in such product forms as powder preparations, emulsion preparations and hydrated preparations. However, these product forms have the following drawbacks. For example, powder becomes a source of pollution because it floats in the breeze when being dispersed. Also, an emulsion preparation not only utilizes a large quantity of organic solvent that causes great concern regarding air pollution, it is also against the concept of conservation of resources. Furthermore, a hydrated preparation has the problem of jeopardizing worker safety from floating powder during the process of hydration with water.

Accordingly, suspension preparations (flowable preparations) have been developed aiming at alleviating these drawbacks. Suspension preparations are preparations that are prepared by formulating surfactants and water-soluble polymers with finely pulverized raw agrochemicals, to give a stable suspended form. A suspension preparation is spread in the same manner as an emulsion preparation, by diluting it in water first, and the same effectiveness as that of an emulsion preparation can be expected. Additionally, since suspension preparations contain almost no organic solvent, there is no concern of adverse effects caused by chemicals compared to emulsion preparations. Furthermore, there is the advantage of no safety concerns with respect to manufacturing, storage and transportation.

Various methods have been tried in order to stabilize the raw substances in the suspended solution for this type of preparation. In one of the methods, surfactants having a dispersing effect and protective colloid agents are incorporated together to appropriately increase the viscosity of the system and prevent separation or sedimentation of the dispersed particles.

As examples of water-soluble polymers serving as protective colloids, gum arabic, sodium alginate, tragacanth gum, dextrin, gelatin, casein, glue, carboxymethylcellulose, methylcellulose, hydroxyethylcellulose, polyvinyl alcohol, polyvinyl pyrrolidone, water-soluble

starch, polysodium acrylate, maleic anhydride-styrene copolymers and maleic anhydride-isobutylene copolymers can be cited. Additionally, it is also well known in the art that water-soluble biopolymer xanthan gum is utilized in agrochemical suspension preparations.

In order to give long-term stability to this type of agrochemical suspension preparation, it is necessary to utilize a large quantity of the aforementioned polymers so that the viscosity of the system can be increased. Also, because the self-dispersing property of the agrochemical suspension preparations is not good after the viscosity is thickened, an agitation device is required when the diluting operation with water is carried out.

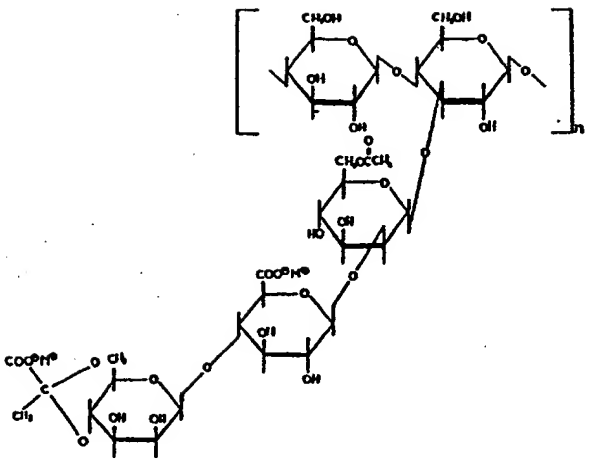
Problems to be solved by the invention

Accordingly, because a large quantity of polymer compound must be incorporated to improve stability, which in turn makes it more difficult to handle the product, the objective of the present invention lies in improving an agrochemical suspension preparation and providing an agrochemical suspension preparation as a product that is easy to handle with excellent suspension stability, fluidity and self-dispersing properties.

Means to solve the problems

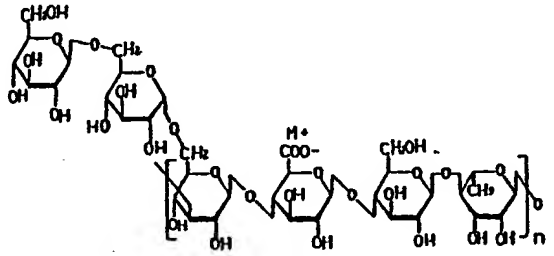
The present inventors conducted rigorous investigations and discovered that, by incorporating surfactants that can provide suspension stability and water-soluble polymers containing carboxy groups into an agrochemical suspension preparation containing biopolymers, the self-dispersing property can be significantly improved, and thus the present invention was accomplished.

The water-soluble biopolymers according to the present invention are fermented polysaccharides such as xanthan gum and rhamsan gum. Xanthan gum is natural gum material obtained by fermentation of glucose with the microorganisms *Xanthomonas* and *Campestris*, followed by purifying polysaccharides accumulating outside the microorganism bodies, which gum is then pulverized. The structure of xanthan gum is shown in the following, where the straight chain comprises 2 glucose units while the side chain comprises 2 mannose units and 1 gluconic acid unit.



M+ represents Na, K or 1/2Ca

Rhamsan gum is a natural gum material obtained by fermentation of glucose with microorganisms of the Alcaligenes sp., ATCC 31961 (registry number in accordance with American Type Culture Collection), followed by purifying the polysaccharides accumulating outside the microorganism bodies, which gum is then pulverized. The structure of rhamsan gum is shown in the following, where the straight chain comprises 2 glucose units and 1 unit each of glucuronic acid and rhamnose, while the side chain comprises 2 glucose units.



M+ represents Na, K or 1/2Ca

By incorporating the aforementioned biopolymers at an extremely small level, the agrochemical suspension preparation shows a remarkable thixotropic property and demonstrates a stabilizing effect for the suspension. The amount of incorporation is 0.02-0.5 wt%, but is particularly preferred at 0.02-0.1 wt%.

Next, as examples of surfactants utilized in the present invention, anionic surfactants such as lignin sulfonate salts, alkylarylsulfonate salts, dialkyl sulfosuccinates, polyoxyethylene

alkylaryl phosphates, polyoxyethylene alkyl aryl ether sulfates, alkylnaphthalene sulfonate salts and polyoxyethylene styryl phenyl ether sulfates, and nonionic surfactants such as polyoxyethylene alkyl aryl ether, polyoxyethylene styryl phenyl ether, polyoxyethylene alkyl ether, polyoxyethylene alkyl ester, polyoxyethylene sorbitan alkylates, polyoxyalkylene glycols and polyoxyethylene styryl phenol ether polymers can be cited, and there is no restriction as to which one is used. They can be utilized alone or as mixture of 2 kinds or more.

Also, water-soluble polymers having carboxy groups and functioning as an agent for improving the self-dispersing property in the present invention comprise carboxymethylcellulose, carboxymethylated starch, polyacrylic acid, maleic anhydride-styrene copolymers and maleic anhydride-isobutylene copolymers.

The aforementioned water-soluble polymers having carboxy groups are materials that can demonstrate the effect of improving the self-dispersing property of agrochemical suspension preparations, and the amount of incorporation is 0.05-5 wt%, but is particularly preferred at 0.1-2 wt%.

Preservatives, fragrances, dyes, etc., may be optionally added to the products of the present invention.

The present invention is specifically explained with application examples below, but the application examples are not to be construed as limiting the scope of the present invention. Here, the parts and % in the application examples are parts by weight and wt%, unless otherwise indicated specifically.

Preparation method A of agrochemical suspension preparation

Composition (I)	Sulfur	50%
	Ethylene glycol	8%
	Surfactant	3%
	Water	39% - (x + y)%
	Biopolymer	x%
	Improving agent for self-dispersing property	y%
		100%

The sulfur, ethylene glycol, surfactant and water of composition (I) and 200 parts of 0.8 mm glass beads with respect to 100 parts of composition (I) were place in a 500 mL beaker, and agitation was carried out for 1 h at 2000 rpm using a Homodisper [transliteration] (product of Nippon Tokusho Kiki K.K.), followed by adding the biopolymer and improving agent for self-dispersing property (water-soluble polymer having carboxy groups) of composition (I) and

mixing-agitating for 1 min at 2000 rpm, to give an agrochemical suspension preparation after removing the glass beads.

Application Examples 1-16 and Comparative Examples 1-10

Agrochemical suspension preparations were obtained following the aforementioned preparation method A, by varying the type and the amount of incorporation of the biopolymer and improving agent for self-dispersing property (water-soluble polymer having carboxy groups) of composition (I) as shown in Table 1 and by using polyoxyethylene distyrylated phenol ether (13 mol EO) as the surfactant.

Table 1 shows the results of the suspension stability and the self-dispersing property of each agrochemical suspension preparation tested by the following evaluation method.

Evaluation method of preparation stability

Agrochemical suspension preparation 20 mL was placed in a 25 mL test tube with a stopper, followed by standing, and the aging stability for 1 month at 10°C and 1 month at 40°C was calculated from the following equation, wherein the greater the number, the worse the stability.

$$\text{Stability} = \frac{\text{Clear separated layer on top (cm)}}{20} \times 100$$

Self-dispersing property

100 mL of 5° hard water were placed in a 100 mL volumetric cylinder, to which one drop agrochemical suspension preparation was added, and the self-dispersing property was observed visually. The expressions are given as follows.

◎: Self-dispersing property is excellent

O: Self-dispersing property is good

Δ: Does not disperse completely and the nondispersed material reaches the bottom of the cylinder

x: Does not disperse at all and all the material settles on the bottom

Table 1

		(1) バイオポリマー		(2) 自己分散性改良剤		(3) 懸濁農薬製剤			
		種類 (4)	添加量 (5) %	種類 (4)	添加量 (5) %	粘度 (6) (cp20℃)	自己分散性 (7)	安定性 (8) (1ヶ月) 10℃	40℃
(9) 実施例	1	キサンタンガム	0.05	セロゲン5A	2.0	550	◎	0	0
	2	〃	〃	〃	1.0	510	◎	0	0
	3	(11)	0.1	〃	1.0	440	◎	0	0
	4	〃	〃	〃	0.5	280	◎	0	1
	5		0.05	セロゲン3H	0.1	240	◎	1	2
	6		〃	〃	0.2	315	◎	0	0
	7		0.1	(13) 〃	0.1	410	◎	0	0
	8		〃	〃	0.2	590	○	0	0
	9	ラムダンガム	0.05	セロゲン5A	0.2	210	◎	1	3
	10	(12)	〃	〃	0.5	290	◎	0	0
	11		0.1	〃	0.1	735	○	0	0
	12		〃	〃	0.5	860	○	0	0
	13		0.02	セロゲン3H	0.1	270	◎	0	1
	14		〃	〃	0.2	450	◎	0	0
	15		0.05	〃	0.1	480	◎	0	0
	16		〃	〃	0.2	680	○	0	0
(10) 比較例	1	キサンタンガム	0.1	——	—	247	×	2	38
	2	〃	0.2	——	—	452	×	0	16
	3	(11) 〃	0.3	——	—	864	×	0	0
	4	ラムダンガム	0.02	——	—	73	◎	50	59
	5	(12) 〃	0.05	——	—	181	○	2	5
	6	〃	0.1	——	—	590	×	0	0
	7	——	—	セロゲン5A	1.0	158	◎	49	57
	8	——	—	(13) 〃	2.0	344	△	21	36
	9	——	—	セロゲン3H	0.1	189	◎	48	55
	10	——	—	〃	0.2	415	△	19	51

Cellogen 5A and 3H are Na salts of carboxymethylcellulose produced by Daiichi Kogyo Seiyaku K.K.

Key:
1 Biopolymer
2 Improving agent for self-dispersion
3 Agrochemical suspension preparation
4 Type
5 Amount of incorporation
6 Viscosity
7 Self-dispersing property
8 Stability (1 month)
9 Application example
10 Comparative example
11 Xanthan gum
12 Rhamsan gum
13 Cellogen ___

Application Examples 17-30 and Comparative Examples 11-15

Agrochemical suspension preparations were obtained following the aforementioned preparation method A, by varying the type and the amount of incorporation of the biopolymer and improving agent for self-dispersing property (water-soluble polymer having carboxy groups)

of composition (I) as shown in Table 2 and by using ammonium polyoxyethylene (13.0 mol EO) distyrylated phenol ether sulfate as the surfactant.

Table 2 shows the test results of the suspension stability and the self-dispersing property of each agrochemical suspension preparation.

Application Examples 31-40 and Comparative Examples 16-20

Agrochemical suspension preparations were obtained following the aforementioned preparation method A, by varying the type and the amount of incorporation of the biopolymer and improving agent for self-dispersing property (water-soluble polymer having carboxy groups) of composition (I) as shown in Table 3 and by using polyoxyethylene (13.0 mol EO) distyrylated phenol ether phosphate as the surfactant.

Table 3 shows the test results of the suspension stability and the self-dispersing property of each agrochemical suspension preparation.

Table 2

		(1) バイオポリマー		(2) 自己分散性改良剤		(3) 懸濁農薬製剤			(8) 安定性 (1ヶ月)	
		(4) 種類	(5) 添加量 %	(4) 種類	(5) 添加量 %	(6) 粘度 (cp20℃)	(7) 自己分散性		10℃	40℃
(9) 実施例	17	(11) キサンタンガム	0.1	(12) 架橋ポリマー(0.5-0.3)	0.5	256	◎		2	3
	18	〃	〃	〃	1.0	310	◎		1	2
	19	〃	〃	〃	2.0	300	◎		1	2
	20	〃	0.2	〃	0.5	460	◎		0	0
	21	〃	〃	〃	1.0	481	◎		0	0
	22	〃	〃	〃	2.0	485	◎		0	0
	23	〃	0.1	ポリアクリル酸ソーダ (MW2万)	0.5	245	◎		1	6
	24	〃	〃	〃	1.0	251	◎		1	6
	25	〃	〃	〃	2.0	254	◎		1	5
	26	〃	〃	〃	3.0	250	◎		1	5
	27	〃	〃	エチレン－無水マレイン酸共重合物部分ナトリウム塩(MW1万)	0.5	241	◎		2	7
	28	〃	〃	〃	1.0	245	◎		1	6
	29	〃	〃	〃	2.0	245	◎		1	6
	30	〃	〃	〃	3.0	249	◎		1	6
(10) 比較例	11	キサンタンガム	0.1	——	—	241	×		2	41
	12	〃	0.2	——	—	462	×		0	19
	13	——	—	架橋ポリマー(DS-0.3)	1.0	45	◎		54	58
	14	——	—	ポリアクリル酸ソーダ (MW2万)	1.0	42	◎		53	57
	15	——	—	エチレン－無水マレイン酸共重合物部分ナトリウム塩(MW1万)	1.0	46	◎		53	56

Key:
1 Biopolymer
2 Improving agent for self-dispersion
3 Agrochemical suspension preparation
4 Type
5 Amount of incorporation
6 Viscosity
7 Self-dispersing property
8 Stability (1 month)
9 Application example
10 Comparative example
11 Xanthan gum

12 CM (carboxymethylated) starch (DS = 0.3)
Sodium polyacrylate (MW 20,000)
Ammonium styrene-maleic anhydride copolymer resin (MW 10,000)

Table 3

		(1) バイオポリマー		(2) 自己分散性改良剤		(3) 懸濁農薬製剤				
		(4) 種類	(5) 添加量 %	(4) 種類	(5) 添加量 %	(6) 粘度 (cp 20℃)	(7) 自己分散性	(8) 安定度 (1ヶ月) 10℃	40℃
(9) 実施例	31	キサンタンガム	0.1	(12) ポリマー5a	0.5	610	◎	0	0
	32	〃	〃	〃	1.0	750	◎	0	0
	33	〃	〃	ポリマー3B	0.1	735	◎	0	0
	34	〃	〃	〃	0.5	982	○	0	0
	35	〃	〃	CM化スターチ(DS=0.3)	0.5	655	◎	0	0
	36	〃	〃	〃	1.0	669	◎	0	0
	37	〃	〃	〃	2.0	704	◎	0	0
	38	〃	〃	イソブチレン－無水マレイン酸共重合物(Mw5万)	0.5	665	◎	0	0
	39	〃	〃	〃	1.0	691	◎	0	0
	40	〃	〃	〃	4.0	702	◎	0	0
(10) 比較例	16	キサンタンガム	0.1	(12) ———	—	620	△	0	41
	17	—	—	ポリマー5a	1.0	168	◎	54	57
	18	—	—	ポリマー3B	0.1	206	○	56	55
	19	—	—	CM化スターチ(DS=0.3)	1.0	49	◎	54	57
	20	—	—	イソブチレン－無水マレイン酸共重合物(Mw5万)	1.0	78	◎	55	59

(11) Rhamsan gum

Key:
1 Biopolymer
2 Improving agent for self-dispersion
3 Agrochemical suspension preparation
4 Type
5 Amount of incorporation
6 Viscosity
7 Self-dispersing property
8 Stability (1 month)
9 Application example
10 Comparative example
11 Rhamsan gum
12 Cellogen ___
CM (carboxymethylated) starch (DS = 0.3)
Sodium isobutylene-maleic anhydride (MW 50,000)

Effect of the invention

The agrochemical suspension preparation of the present invention can be produced with a small quantity of polymer compounds, affording products having excellent fluidity, self-dispersion and stability properties for easy handling.